# NONCONVENTIONAL FRIEDEL–CRAFTS CHEMISTRY.
# VIII. ON THE PREFERENTIONAL INTRAMOLECULAR CYCLIZATION REACTIONS OF 2-ARYL-2-BENZYL-1,3-OXATHIOLAN-5-ONE UNDER LEWIS ACIDS CATALYTIC ACTION

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Received April 16, 1992
Accepted October 19, 1992

In our previous work, we reported the intermolecular reactions of spirothialactones with arenes[1], ferrocene[2] and thiophene[3]. The results of these investigations together with our interest in Friedel–Crafts chemistry[4 – 10] prompted us to consider the intramolecular cyclization reactions of 2-aryl-2-benzyl-1,3-oxathiolan-5-one derivatives (*IIa – IId*) under Lewis acid catalysts effect.

## EXPERIMENTAL

Melting points are uncorrected. NMR spectra were measured on EM-360 90 MHz spectrometer in $(CD_3)_2SO$ unless other specified. Infrared spectra were recorded in KBr on a Pye–Unicam SP 200-G spectrophotometer. UV absorbances were measured on a Perkin–Elmer 552 spectrophotometer. GC/MS analyses were performed on a Finnigan 4023 quadrupole system equipped with Model 4500 source upgrade, using a 50 m DB-1 fused silica WCOT capillary column with a film thickness of 0.25 μm. Mass spectra were determined on Dupont 21-49 mass spectrometer equipped with data system.

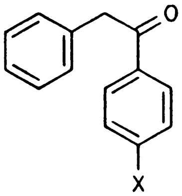
HPLC analyses were performed on a Hitachi apparatus (Japan) supplied with a variable wavelength monitor (190 – 600 nm) with a sulfonated silica gel type column, Nucleosil 55A and methanol–water mixtures as a solvent.

### Preparation of 2-Aryl-2-benzyl-1,3-oxathiolan-5-one (*IIa – IId*): General Procedure

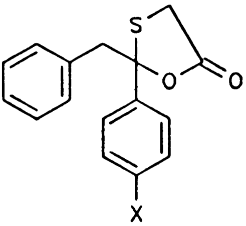
A mixture of 0.1 mol of deoxybenzoines (*Ia – Id*) and 0.1 mol of thioglycolic acid was dissolved in 200 ml dry benzene, to this solution was added catalytic amount of *p*-toluenesulfonic acid then the reaction mixture was refluxed on a water bath whereby the calculated volume of liberated water was removed using water separator. After the completion of the reaction (TLC), the solution was concentrated and the reaction mixture was poured in evaporating dish whereby the precipitated product was collected by filtration, and dried to afford compounds (*IIa – IId*).

### Reaction of 2-Aryl-2-benzyl-1,3-oxathiolan-5-one (*IIa* – *IId*) in the Presence of $AlCl_3$ Catalyst; General Procedure

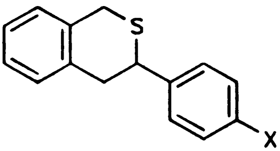
$AlCl_3$ (4.4 mmol) was added to a solution of 10 mmol of *IIa* – *IId*, respectively, in nitromethane or carbon disulfide. The reaction mixture was stirred for 24 h at room temperature, decomposed with 10% HCl solution, and extracted with chloroform and methylene chloride; the combined extracts were washed with water, 10% sodium carbonate solution, water and dried over magnesium sulfate. The solvents were removed on rotary evaporator and the residue was subjected to GC/MS and HPLC analyses and to separation and purification by preparative thin layer chromatography on silica gel. Products were indentified, results are presented in Table I.



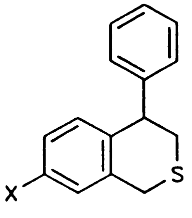
*I*



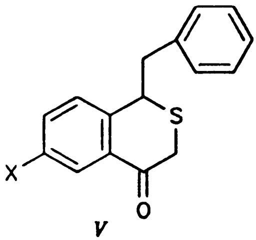
*II*



*III*



*IV*



*V*

In formulae *I*–*V*: *a*, X = H
*b*, X = $CH_3$
*c*, X = $OCH_3$
*d*, X = Cl

TABLE I
Physical data of the synthesized compounds *II* – *V*

| Compound | Formula (M. w.) | M. p., °C Yield[a], % | Calculated/Found % C | % H | % Cl | % S | IR, cm$^{-1}$ | $^1$H NMR |
|---|---|---|---|---|---|---|---|---|
| *IIa* | $C_{16}H_{14}O_2S$<br>(270.1) | 69 – 71[b]<br>75 | 71.11<br>70.85 | 5.18<br>5.00 | | 11.85<br>11.40 | 700 (C–S), 1 265, 1 320 (C–O), 1 725 (C=O), 2 920 (CH aliph.), 3 050 (CH arom.) | 3.6 s, 2 H; 3.9 s, 2 H; 7 – 7.70 m, 10 H |
| *IIb* | $C_{17}H_{16}O_2S$<br>(284.3) | 120 – 122[b]<br>80 | 71.83<br>71.50 | 5.63<br>5.30 | | 11.26<br>10.95 | 710 (C–S), 1 265, 1 320 (C–O), 2 850 (CH aliph.), 3 030 (CH arom.) | 2.3 s, 3 H; 3.6 s, 2 H; 3.8 s, 2 H; 7 – 7.60 m, 9 H |
| *IIc* | $C_{17}H_{16}O_3S$<br>(300.1) | 158 – 160[b]<br>82 | 68.00<br>67.75 | 5.33<br>5.00 | | 10.66<br>10.25 | 710 (C–S), 1 265, 1 325 (C–O), 1 725 (C=O), 2 920 (CH aliph.), 3 035 (CH arom.) | 3.4 s, 2 H; 3.6 s, 3 H; 3.8 s, 2 H; 7 – 7.8 m, 9 H |
| *IId* | $C_{16}H_{13}O_2ClS$<br>(304.4) | 170 – 172[b] dec.<br>65 | 63.15<br>63.00 | 4.27<br>4.00 | 11.51<br>11.30 | 10.52<br>10.20 | 700 (C–S), 1 265, 1 320 (C–O), 1 720 (C=O), 2 930 (CH aliph.), 3 050 (CH arom.) | 3.2 s, 2 H; 3.6 s, 2 H; 7 – 7.8 m, 9 H |
| *IIIa*[g] | $C_{15}H_{14}S$<br>(226.3) | viscous oil[c]<br>40 | 79.64<br>79.20 | 6.19<br>6.00 | | 14.15<br>14.00 | 700 (C–S), 2 920 (CH aliph.), 3 050 (CH arom.) | 3.9 d, 2 H; 4.5 s, 2 H; 4.8 t, 1 H; 7 – 7.8 m, 9 H |
| *IIIb*[g] | $C_{16}H_{16}S$<br>(240.2) | 43 – 45[d]<br>45 | 80.00<br>79.70 | 6.66<br>6.32 | | 13.33<br>13.00 | 710 (C–S), 2 920 (CH aliph.) 3 050 (CH arom.) | 2.4 s, 3 H; 3.9 d, 2 H; 4.3 s, 2 H; 4.8 t, 1 H; 7 – 7.75 m, 8 H |
| *IIIc* | $C_{16}H_{16}OS$<br>(256.2) | 47 – 49[d]<br>40 | 75.00<br>74.70 | 6.25<br>6.00 | | 12.50<br>12.20 | 700 (C–S), 1 265, 1320 (C–O), 2 920 (CH aliph.), 3 050 (CH arom.) | 3.7 s, 3 H; 4.1 d, 2 H; 4.4 s, 2 H; 4.7 t, 1 H; 7 – 7.8 m, 8 H |
| *IIId*[g] | $C_{15}H_{13}ClS$<br>(260.5) | 42 – 44[e]<br>30 | 69.23<br>69.00 | 5.00<br>4.70 | 13.46<br>13.25 | 12.30<br>12.00 | 700 (C–S), 2 925 (CH aliph.), 3 050 (CH arom.) | 3.8 d, 2 H; 4.0 s, 2 H; 4.8 t, 1 H; 7 – 7.8 m, 8 H |

TABLE I
(*Continued*)

| Compound | Formula (M. w.) | M. p., °C Yield[a], % | Calculated/Found | | | | IR, cm$^{-1}$ | $^1$H NMR |
|---|---|---|---|---|---|---|---|---|
| | | | % C | % H | % Cl | % S | | |
| *IVa*[g] | $C_{15}H_{14}S$ | 35 – 37[e] | 79.64 | 6.19 | | 14.15 | 710 (C–S), 2 895 (CH aliph.), | 3.8 d, 1 H; 4.2 s, 2 H; 4.6 t, 1 H; |
| | (246.2) | 30 | 79.35 | 6.00 | | 14.00 | 3 030 (CH arom.) | 7 – 7.8 m, 9 H |
| *IVb*[g] | $C_{16}H_{16}S$ | 46 – 48[e] | 80.00 | 6.66 | | 13.33 | 700 (C–S), 2 900 (CH aliph.), | 2.4 s, 3 H; 3.8 d, 2 H; 4.3 s, 2 H; |
| | (240.7) | 30 | 79.60 | 6.24 | | 13.00 | 3 050 (CH arom.) | 4.6 t, 1 H; 7 – 7.70 m, 8 H |
| *IVc*[g] | $C_{16}H_{16}OS$ | 50 – 52[e] | 75.00 | 6.25 | | 12.50 | 710 (C–S), 1 320 (C–O), 2 895 | 3.4 s, 3 H; 3.9 d, 2 H; 4.5 s, 2 H; |
| | (256.8) | | 74.70 | 6.00 | | 12.20 | (CH aliph.), 3 030 (CH arom.) | 4.7 t, 1 H; 7 – 7.8 m, 8 H |
| *IVd* | $C_{15}H_{13}ClS$ | 47 – 49[d] | 69.23 | 5.00 | 13.46 | 12.30 | 700 (C–S), 2 920 (CH aliph.), | 3.9 d, 2 H; 4.3 s, 2 H; 4.6 t, 1 H; |
| | (260.4) | | 69.00 | 4.70 | 13.20 | 12.00 | 3 030 (CH arom.) | 7 – 7.8 m, 8 H |
| *Va*[g] | $C_{16}H_{14}OS$ | 70 – 72[b] | 75.59 | 5.51 | | 12.59 | 710 (C–S), 1 715 (C=O), 2 890 | 3.6 d, 2 H; 4.4 s, 2 H; 4.9 t, 1 H; |
| | (254.2) | 7 | 75.25 | 5.30 | | 12.40 | (CH aliph.), 3 050 (CH arom.) | 7 – 7.8 m, 9 H |
| *Vb*[g] | $C_{17}H_{16}OS$ | 75 – 77[f] | 76.11 | 5.97 | | 11.94 | 700 (C–S), 1 720 (C=O), 2 920 | 2.4 s, 3 H; 3.6 d, 2 H; 4.3 s, 2 H; |
| | (268.5) | 5 | 76.00 | 5.60 | | 11.65 | (CH aliph.), 3 035 (CH arom.) | 4.8 t, 1 H; 7 – 7.7 m, 8 H |
| *Vc* | $C_{17}H_{16}O_2S$ | 80 – 82[b] | 71.83 | 5.63 | | 11.26 | 710 (C–S), 1 720 (C=O), 2 895 | 3.7 s, 3 H; 3.9 d, 2 H; 4.3 s, 2 H; |
| | (284.3) | 4 | 71.50 | 5.30 | | 11.00 | (CH aliph.), 3 050 (CH arom.) | 4.9 t, 1 H; 7 – 7.6 m, 8 H |
| *Vd* | $C_{16}H_{13}ClOS$ | 88 – 90 | 66.66 | 4.51 | 12.15 | 11.11 | 710 (C–S), 1 715 (C=O), 2 890 | 3.9 d, 2 H; 4.1 s, 2 H; 4.7 t, 1 H; |
| | (288.1) | 4 | 66.30 | 4.20 | 12.00 | 11.00 | (CH aliph.), 3 030 (CH arom.) | 7 – 7.8 m, 8 H |

[a] Calculated from HPLC; crystallized from: [b] ethanol, [c] petroleum ether, [d] dichloromethane–petroleum ether (1 : 4), [e] methanol–water (1 : 3), [f] methanol; [g] NMR measured in $CDCl_3$.

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